Charis M. Galanakis *Ed.*

Trends in Sustainable Chocolate Production

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Preface

Chocolate is an extremely popular delicacy that is continuously consumed worldwide by people of all ages due to its sensory characteristics. On the other hand, the awareness of modern consumers about the link between healthy eating and well-being is changing their consuming habits in foods that generate positive organoleptic feelings and are also supported by sustainable supply chains. Besides, sustainability is becoming an essential item for the food industry worldwide as resources become more restricted and demand grows. However, most books on the market cover chocolate manufacture, without considering sustainable practices of production, consumption, and market aspects.

Food Waste Recovery Group (www.foodwasterecovery.group) has developed several activities, including consultation reports to different governmental, industrial, and research bodies, workshops, webinars, e-courses, publications, a new open-access journal (*Discover Food*, Springer Nature), and multiple books in the broad fields of food, nutrition, bioresources, and environment. Following these efforts, the current book fills the knowledge transfer gap between academia and industry by covering all the essential aspects of the chocolate industry (manufacture, functionality, sustainability of the supply chain, commercialization aspects, and market characteristics) in one reference. The ultimate goal is to support the scientific community, professionals, and enterprises that aspire to develop a sustainable chocolate sector.

The book consists of ten chapters. **Chapter 1** deals with the state-of-the-art harvesting and post-harvest handling of cacao and provides an update on chocolate manufacturing and the impacts of processing on chocolate's sensory and functional quality. Chocolate production implies an extensive post-harvest process of the cacao beans, the seeds of the tree *Theobroma cacao* L. All the steps from bean harvesting into the chocolate bar's development affect chocolate properties, providing to the final product unique sensory qualities that will attract consumers.

Chapter 2 provides a comprehensive overview of the origins, processing, quality control, and flavor development of cocoa beans. Significant cocoa flavor markers are theobromine, caffeine, catechin, epicatechin, and proanthocyanidins. However, cocoa flavor notes are built upon intricate combinations of amino acids, alcohols, phenols, volatile acids, esters, aldehydes, ketones, lactones, terpenoids, minerals, glycated and polymeric substances.

The chocolate industry and cocoa products undergo intense competition and evolution, which demands new food products. In **Chapter 3**, the ways to improve the functional characteristics of the chocolate products are reviewed. Calorie reduction in chocolates using sugar and cocoa butter alternatives and its effect on chocolate quality is also denoted. In addition, the influence of processes applied for cocoa and chocolate productions on polyphenol composition and antioxidant activity is summarized. The growing demand for functional food from sustainable plant-based produce motivates food scientists to develop new types of chocolate products containing vegetal extract. The incorporation of vegetal extract in the chocolate formulation is intentionally aimed to improve the health-promoting properties of the chocolate, such as phenolic content and antioxidant activity. Herbs and spices are some other ingredients with potential use in the chocolate formula. To this line, **Chapter 4** presents the various bioactive compounds in cocoa, the impact of chocolate processing on the bioactive compounds of cocoa, enhancing the bioactive components of chocolate by incorporating different vegetal extracts, and the consumer perception of chocolate and chocolate with vegetal extracts.

Chapter 5 focuses on the phase transition of tempered and non-tempered dark chocolate processed with cocoa from different geographical origins, using differential scanning calorimetry, rheometry, and thermography. Cocoa butter plays a vital role in the appearance and texture of chocolate, and the polymorphic forms in the final product depend on the tempering process. The fatty acids profile does not present significant differences related to the geographical origin, with higher values for palmitic acid, stearic acid, and oleic acid. However, the phase transition is influenced by the tempering process.

Since consumers have become aware of different cocoa genotypes and their origins, which caused an expanding market of premium chocolates with single-origin cocoa beans, cocoa beans may be subjected to adulteration due to the high demand for superior quality products. Therefore, for the accurate discrimination of the cocoa beans, three major analytical approaches can be implemented: (1) chemical approaches, (2) biomolecular approaches, and (3) isotopic approaches. In **Chapter 6**, these three approaches are reviewed together with the recent literature on traceability of cocoa origin.

Nowadays, the increase in the global demand for chocolate production changes the production systems of this agri-food product. Although chocolate production is increasing daily, this volume production leads to a substantial environmental cost due to changes in production systems. Given the awareness of the irreparable ecological consequences, there is currently significant interest in producing and consuming sustainable food products such as chocolate. To better understand the environmental impacts of the life cycle of chocolate, **Chapter 7** provides an overview of the environmental impacts of chocolate production throughout its life cycle. Also, it reviews and compares the environmental problems of chocolate production and presents a clear picture of future perspectives which should be considered in the production of chocolate.

Chapter 8 examines the discourse of corporate sustainability efforts for cocoa sourcing, using Ghana as an example. Taking nothing away from the sincerity or insincerity of corporate sustainability efforts, the chapter underlines the disconnect of values, motivations, and benefits between corporate sustainability for now and local people's sustainability in perpetuity that threatens the UN's Sustainable Development Goals (SDGs) generally.

Chapter 9 identifies the more widely used sustainability labels in chocolate and investigates the relation between chocolate labeling and purchase intention and perception. The results conclude that sustainability labeling information influences consumers' purchase decisions and sensory scores. Hence, many consumers worldwide are willing to pay extra money for cocoa and chocolate manufactured following ethical principles and, thus, with sustainability labels on the packaging.

Finally, **Chapter 10** characterizes the chemical composition of the residual cocoa biomass and explores the existent valorization strategies. Based on the composition (polyphenols, organic acids, methylxanthines, etc.) of this by-product, valuation strategies applied to different fields, such as the food industry, human health, cosmetics, and bioremediation, are proposed for each one. These advances would help improve some socio-economical and environmental indicators and promote the sustainability of the world's cocoa production chain.

Conclusively, the current book is expected to assist food scientists and technologists, researchers and professionals working in the edge of the food and environmental field, and agriculturalists and food engineers, who seek to improve the efficiency of production systems. It also concerns specialists working in the chocolate industry, from farm to fork. It could also be purchased by University Libraries and Institutes all around the world to be used as a textbook and/or ancillary reading in under-graduates and post-graduate level multi-discipline courses dealing with sustainable food systems, agricultural and environmental science, and food processing.

At this point, I would like to acknowledge and thank all authors for accepting my invitation. Their dedication to the project, timeline, and editorial guidelines are highly appreciated. I would also like to thank the acquisition editor Daniel Falatko, book manager Arjun Narayanan, and all the production team of Springer Nature for their help during this book's preparation. Last but not least, I have a message for all the readers. This kind of book project is a collaborative effort containing hundreds of thousands of words, and it may contain errors. Constructive comments and even criticism are always welcome, so do not hesitate to get in touch with me to suggest any changes.

Chania, Greece Charis M. Galanakis

Contents

Chapter 1
State-of-the-Art Chocolate Manufacture

Marcela Hernández-Ortega, Carla Patricia Plazola-Jacinto, and Lourdes Valadez-Carmona

Abstract Chocolate production implies an extensive post-harvest process of the cacao beans, the seeds of the tree *Theobroma cacao* L. All the steps from bean harvesting into the chocolate bar's obtention (cocoa origin, composition and manufacturing procedure) will affect chocolate properties, providing to the final product unique sensory qualities that will attract consumers. Cocoa products are worldwide consumed because they are recognized as a significant source of polyphenols, molecules with essential health benefits. The current consumers' concern about their wellness leads them to change the purchasing behavior and looking for new beneficial health-related products. In this context, and in addition to its sensorial properties chocolate rich in cacao content is an exceptional carrier to deliver bioactive compounds such as flavonoids, tannins, peptides, fiber, and some probiotics among others; making the chocolate a good healthy product. For this reason, this chapter aims to provide an update on the harvesting, post-harvest handling of cacao, chocolate manufacturing, and how each process impacts the sensorial and functional quality of chocolate.

Keywords Cacao bean · Chocolate · Epicatechin · Methylxanthines · Mood

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1.1 Introduction

Cacao (*Theobroma cacao* L.) belongs to Sterculiaceae family and is also called "Food of God". Cacao is widely distributed in tropical countries mainly in those of the equatorial region such as Cote d'Ivory (32.2%), Ghana (19.3%), Indonesia (16.4), Brazil (6.2), Cameroon (6.1), Nigeria (5.6%), and others with less production (Dinarti et al., 2015; Li et al., 2019). Cacao is economically significant because it is the raw material for chocolate, liquor, cocoa powder and cacao butter manufacture for confectionery, food and cosmetic industries (Dinarti et al., 2015; Rojas et al., 2020). According to the World Cocoa Foundation ICCO, annual global cacao production was more than four million tons (Kongor et al., 2016; Valadez-Carmona et al., 2017) of which 90% are produced by five to six million farmers in developing countries. The cacao tree is a perennial and non-climacteric tree with five-year generation time, after this the tree has continuously production throughout the year. Cacao tree grows best in hot and moisture conditions; in drought conditions vegetative and reproductive functions are depressed (Kongor et al., 2016). Cacao pods emerge from flowers as an extension; the ovules of 15 to 17 old week pods begin solidifying until a developed enlarge and deepen seeds/beans of violet color during the last eight weeks (Li et al., 2019).

When the pods are mature the cacao fruit is constituted by the shell, mucilage, and beans (Fig. 1.1). The shell is made up of 3 well differentiated layers; (1) the exocarp which is spongy and soft; (2) the mesocarp, comprises of hardy semi-woody cells which vary according to the genotype; and (3) the endocarp which is smoothly and fleshy attached to the mucilage. The cacao fruit contain around 30 to 40 beans embedded in a mucilaginous pulp which are extracted from the pod. Farming practices and genus of cacao influence the beans' quality parameters such as size, shape, appearance, and exterior color (Araujo et al., 2019; Armengot et al., 2020; Gutiérrez, 2017; Kongor et al., 2016).

In fact, harvesting factors such as the genotype, geographic and edaphoclimatic conditions as well as the maturity stage influence on physical, nutritional, and phytochemical characteristics of cacao beans. While post-harvesting processing such as fermentation, drying and toasting influences flavor and aroma development.

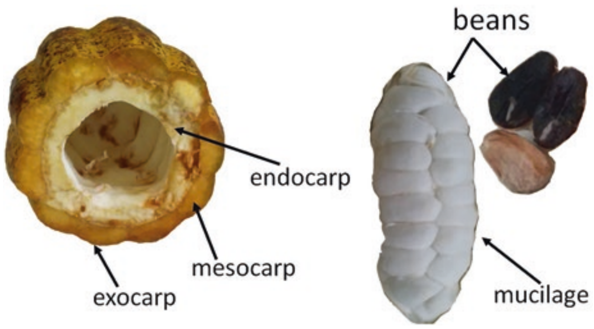


Fig. 1.1 Structure of cacao fruit

(Pérez et al., 2009). Besides cacao's economic importance as a crop, chocolate and cacao derived products have health-related benefits confirmed in *in vitro* studies. The health benefits such as anti-carcinogenic, vasodilatory, antidiabetic, and anti-atherogenic properties have been attributed to the bioactive compounds like polyphenols mainly to the catechin family, which exhibits antioxidant properties (Ioannone et al., 2015; Nguyễn et al., 2018; Rojas et al., 2020; Gutiérrez & Pérez, 2015; Nazaruddin et al., 2006).

The differences between cacao varieties and origin of the cacao beans influence strongly the aroma, phenolic content, volatile compounds, mineral and biochemical composition, pH, total acidity, simple carbohydrates, lipids, proteins, alkaloids.

1.2 Cacao Cultivar Systems

Cacao production is estimated over four million tones around the world (Araujo et al., 2019), and 90% is produced by smallholders (Dinarti et al., 2015). There are two principal cultivar systems that have been used to make cacao: (1) shaded, which is the traditional cacao cultivar system and produces high quality product, and (2) full-sun monocultures which improves the cacao production. Both cultivar systems have benefits to the farmers, thus, to select the plan that fits better to the farmer is necessary to consider all the variables involved in the production (Pérez-Neira et al., 2020; Somarriba & López Sampson, 2018; Useche & Blare, 2013).

Agroforestry is defined as "the intentional integration of trees and shrubs into crop and animal farming systems to create environmental, economic, and social benefits" (Muschler, 2016). In this context cacao might be produced using different agroforestry practices. It differs in the crop husbandry cover intensity and allows combining forestry and agricultural production on the same area.

These practices are classified as follows: (1) forest-like systems in which cacao is included in the natural forest ecosystem, (2) mix shade systems in which are included various shade trees that varies in size, (3) productive shade systems, (4) specialized shade systems, (5) open sun, and (6) no-shade systems; the two latter decrease the forest cover and intensified the agricultural land use leading to a deforestation (Somarriba & López Sampson, 2018). When diverse varieties of leguminous, fruit trees, palm, and timber trees are included in the agroforestry system they provide natural nitrogen fixing to nourish the soil (Armengot et al., 2020; Muschler, 2016; Useche & Blare, 2013; Wartenberg et al., 2020; Wickramasuriya & Dunwell, 2018). The agroforestry creates right microclimate conditions such as reduction of wind speed and light availability, increment of relative humidity and buffered temperatures of the cultivar area with environmental benefits such as the nutrient cycle, pest and disease regulation, and biodiversity conservation (Wartenberg et al., 2020). Besides, it also provides a social, cultural, and economic impact to the farmers and the surrounding's rural livelihoods; all of these benefits derived from the architecture and spatial arrangement of cacao trees that mimics the native forest and limits the land to other agricultural uses (Clough et al., 2009; Pérez-Neira et al., 2020; Useche & Blare, 2013).

Agroforestry systems can offer both (1) planned biodiversity, which is associated with the crops and may vary according to farmer management; and (2) the associated biodiversity in which is included flora, fauna, and microorganisms that may colonize the land from surroundings (Useche & Blare, 2013). It is estimated that shaded cacao cultivar represents 85% of the cultivars in Latin America. The agroforestry cacao system synergizes the associated biodiversity and the planned biodiversity creating a welcoming environment and additional species. However, this practice has diminished and currently it represents only 31% of the total global cultivated area (Somarriba & López Sampson, 2018; Somarriba et al., 2012).

In contrast both the increasing demand of chocolate, and the decrease in the productivity of aging trees had incentive the exploitation of land converting most of the forest into cacao farmlands (Hebbar et al., 2020). This, transformed the traditional shaded cultivar to full-sun monocultures, which have higher yields and profits than shade cultivars in a short period (Pérez-Neira et al., 2020, Useche & Blare, 2013). The implementation of full-sun monoculture has some benefits to the farmers as high yield productivity in short term (kg and/or \$ ha^{-1}), due to the modernization of the production systems and the labor inputs. However, these benefits go along with some drawbacks as the increase and dependence on non-renewable energy consumption and the loss of the genetic variability due to the replacement of local varieties for genetically uniform types (Pérez-Neira et al., 2020, Useche & Blare, 2013). This loss in genetic variability increases the vulnerability of the crop to environmental changes, weeds, pest and pathogens development, exacerbating the use of herbicides and pesticides for their management and synthetic fertilizers for nutrient deficiency (Pérez-Neira et al., 2020; Useche & Blare, 2013).

The consumers' recent environmental degradation awareness has changed their purchasing behavior and demands organic, green and sustainable products with fair trades. This market tendency indirectly has renewed the interest of producers to reinvert their time in agroforestry practices such as periodical removal of diseased pods, drainage systems maintenance and pruning of cacao trees (Armengot et al., 2020). This tendency in the market has also indirectly renewed the producers' interest to reinvert their time in agroforestry practices by higher cacao prices that compensate for the extra labor. Therefore, the development of eco-labels, specific certifications and denomination of origin with strict environmental production standards encourage farmers to access to an alternative, distinctively and certified market niches, improving their economy besides reforesting their agricultural areas (Armengot et al., 2020; Somarriba & López Sampson, 2018; Useche & Blare, 2013). Contrary to the farmers' beliefs, acceptable cultivar management practices either in agroforestry or monocultures impact on the cacao yield, reducing the number of the diseased pod when a periodical removal of the diseased pods are done. Armengot et al. (2020) observed that frosty diseased pods lower than 18% were cut in the sporulation phase. These practices may avoid deforestation of the land and may increase the farmers' environmental non-market benefits.

Although the economic benefits, yet the small farmers' have to consider several variables to choose what type of agricultural systems adapted best to their necessities. Various authors proposed and analyzed different models (Hayes, 2008; LeClair, 2008). Nonetheless, only consumer-worker utility models were taking into account and, the relationship producer-consumer-worker were not included in the development of a decision model. These models did not consider the effect of the price premium on the producers and did not consider the ecological impact. Therefore, Useche et al. developed a farm-household model in which they considered the market benefits of the production and the associated environmental non-market benefits to the production. Useche and Blare (2013), focused on the planned biodiversity effects on household behavior, emphasizing the non-market ecological economy's valuing the biodiversity and environmental questions.

Useche and Blare (2013) model approaches consider estimating both the crash crop and the production of planned biodiversity. This model was applied to Ecuadorian cacao production observing a compensatory effect in different product markets, labor market limitations, and differences in market and shadow wages derived from the environmental benefits associated with planned biodiversity management.

1.3 Factors That Affect the Cacao Beans' Quality

Several physical and biochemical indicators are used to evaluate the quality of cacao beans: size, amount, color, acidity, amount and type of volatile compounds and polyphenols, among others (Kongor et al., 2016). These indicators are affected by environmental growth conditions (soil chemical composition, temperature, moisture, etc.), maturity grade, postharvest treatment, and chocolate manufacture processing.

1.3.1 Environmental Factors

The type of cultural system influences the quality of cacao, it has been reported that soil and climatological conditions have positive or negative impacts on the cacao quality such as flavor, aroma, and biochemical composition of cacao beans, which determined the kind of market in which will be sold.

The shade cacao cultivars in humid tropics contribute positively to carbon storage, nutrient cycle, and reforestation. Cacao trees grow in coarse particle soils rich in nutrients and a depth of 1.5 m, allowing them to develop a sound root system (Kongor et al., 2016). The soil structure is commonly as aggregates important on soil organic matter storage (SOM) which protects the organic matter compounds from a rapid degradation. The remaining plants, animals, and microorganisms are the principal organic matter found in soil which, is degraded gradually, releasing the nutrients to be uptake by cocoa trees (Wartenberg et al., 2020). Besides the soil structure the balance of cationic and anionic compounds in the soil is vital to avoid nutritional problems that affect cacao quality. The cation exchange capacity (CEC) indicates the soil's ability to absorb and release cations (e.g., Ca+, Mg2+, and K+). According to the International Cocoa Organization ICCO (2013), the optimal total nitrogen-total phosphorus ratio should be 1.5. It has been reported that shade cacao cultivars increase C concentrations by 6%, compared to open cultivars. Wartenberg et al. (2020) observed that C was much higher under rambutan (3.6 g C kg^{-1} ± 1.1 g C kg^{-1}) compared to other species (jackfruit, guava, mango and coconut). Similar effects were observed on N and P concentration, however the increase in C, N and P may vary depending on the type of shade tree species. In this context the soil's water retention and drainage properties are also crucial for cacao tree growth due to it is susceptible to lack of water. Another factor to consider is the pH of the soil that influences the solubility of minerals and nutrients. A pH in a range of 5-0-7.5 is ideal for cacao tree growth (Dogbatse et al., 2020; ICCO, 2013). However, a too acid ($pH < 4$) or too alkaline ($pH > 8$) soil has to be avoided. A temperature rate of 31–35 °C is the optimal for photosynthesis in cocoa (Balasimha et al., 1991; Hebbar et al., 2020; Yapp, 1992); a rainfall rate between 1400- and 2000-mm $year^{-1}$ is sufficient to maintain a profitable growth of cacao.

Besides C, N and P soil's concentration the carbon dioxide (CO_2), rainfall, and temperature are crucial to seedling and productivity. Hebbar et al. (2020) evaluated under controlled conditions the interaction effect of the CO_2, high temperatures and water deficit on growth, photosynthesis, and WUE observed that elevated CO_2 concentration in the cultivars have a positive effect on the plant's height; 550 and 700 ppm CO_2 produce plants of 1.64 m and 1.71 m respectively. Similar effects were observed to photosynthesis which increased 10% at 550 ppm and 29% at 700 ppm CO_2. In contrast a water deficit at 50% negatively affects the plant height, it decreased 6% and 19% at 550 and 700 ppm CO_2 respectively.

Besides, Dogbatse et al. (2020) studied the growth and nutrient uptake of different acidic soils in Ghana. All the grounds evaluated were sandy clay loam and were adequate to hold water, thus, maintaining the moisture needed for the plant. However, their pH was acid ranging from 4.21 to 5.66 attributable to low exchangeable cations mainly Ca, which may mitigate the toxicity cause by Al concentrations. The soils had high concentrations of both P and K, probably due to the soil's pH (5.5) and to the high levels of clay in the soils respectively (Dogbatse et al., 2020).

These findings highlight the importance of the soil characteristics such as structure and chemical composition for cacao cultivars that may enhance growth, yield, and flavor and aroma compounds development.

1.3.2 Genetic Factors

The type of cultivar, climate, and the soil where cacao grows influence the cacao bean quality, genetic, and variety are also important factors to be considered (Gutiérrez, 2017). The cacao tree is a diploid specie ($2n = 2x = 20$), with genotypes range from 411 Mb to 494 Mb. Ten genetically differentiated populations of the cacao tree have been identified (Amelonado, Contamana, Criollo, Curaray, Guiana, Iquitos, Marañon, Nacional, Nanay and Purús) (Argout et al., 2017; Hämälä et al., 2020; Schwarzkopf et al., 2020; Wickramasuriya & Dunwell, 2018). All of them originating from diverse locations in Central and South America. Guiana shows lower genetic diversity among the others and presents high similarity to Marañon than either Nanay or Iquitos varieties. These ten populations are significantly different among them due to strong signatures of differentiation. Criollo and Amelonado varieties are characterized for being highly self-fertilized, contrary to Iquitos and National Ecuadorian cacao which have low self-fertilization frequency. (Schwarzkopf et al., 2020). Although cacao is genetically diverse and more than 14,000 varieties are known; the main commercial species to manufacture chocolate are Forastero, Trinitario, and Criollo (Gutiérrez, 2017; Rojas et al., 2020; Aprotosoaie et al., 2016). The principal differences among the commercial varieties are the geographic origin, fruit morphology and flavor characteristics.

Criollo (*Theobroma cacao* L. ssp. *cacao* Cuat) is cultivated since pre-Columbian times in Central America, mainly by the Mayans. Nowadays, Criollo trees are grown only in Central America, Venezuela (largest producer), Madagascar, Sri Lanka, and Samoa. Some physical characteristics of Criollo cacao are pod yellow or red when is ripe, large, rounded beans, and white-colored cotyledons. Generally, Criollo cacao is susceptible to both pest damage and climatic changes producing low yields. Criollo cacao is highly appreciated by national and international chocolatiers and the chocolate industry to manufacture fine chocolate due to its aroma and flavor characteristics. The latter may develop flavors like mild, nutty, earthy, flowery, or tea-like (Aprotosoaie et al., 2016; Gutiérrez, 2017; Gutiérrez & Pérez, 2015).

Forastero (*Theobroma cacao* L. ssp. *Shaerocarpum* Cuat), is a variety cultivated in West Africa and South America. It is integrated by several subvarieties, being Amelonado the most known. The group is divided into bulk, necessary and ordinary sub-groups used to produce different cacao derived products. Bulk Forastero represents over 90% of the world production and has large genetic variability it is used for breeding over the world (Aprotosoaie et al., 2016).

Trinitario is a hybrid resulted from Criollo and Forastero varieties. It is cultivated in South America, Central America and in the West Indies. Producers used Trinitario because it is less susceptible to diseases and has higher yields than the other varieties. Trinitario is characterized by a robust raw chocolate and some wine-like flavors (Aprotosoaie et al., 2016).

In this context, Schwarzkopf et al., (2020) evaluated the recombination rates in distinct cacao populations. They observed an overlapping in the recombination hotspots location across the populations; moreover, their results supported the hypothesis of increased recombination rates in domesticated plants such as Criollo cacao (Schwarzkopf et al., 2020).

Derived the increased demand for cacao and the sustainable production, governments have developed programs to improve cacao production through rehabilitation, intensification, and propagation by cacao clones. These programs are focused on the use of disease-resistant and high-yield clones. In this context, the chocolate industry and international organizations subsidized by the Indonesian government have implemented breeding programs to produce superior clones of cacao through embryogenesis. Significantly 53 farmer selections from Sulawesi were analyzed for genetic identity and parentage; finding that farmer selections are comprised of hybrids for three groups of cacao germplasm: Trinitario and two Upper Amazon Forastero groups (Dinarti et al., 2015). In 2004 ICCO developed the program "Cocoa germplasm utilization and conservation: a global approach" in collaboration with different countries (Brazil, Cameroon, Cote D'Ivoire, Ecuador, Ghana, Malaysia, Nigeria, Papua New Guinea, Trinidad And Tobago, and Venezuela). The objectives were international hybrid selection, germplasm conservation, and enhancement particularly for pest and disease-resistant cacao varieties. The project results were the obtention of promising local clones used for breeding, and successful germplasm enhancement for Phytophthora pod rot resistance in Trinidad and Tobago.

1.3.3 Harvesting and Post Harvesting Processing

1.3.3.1 Maturity

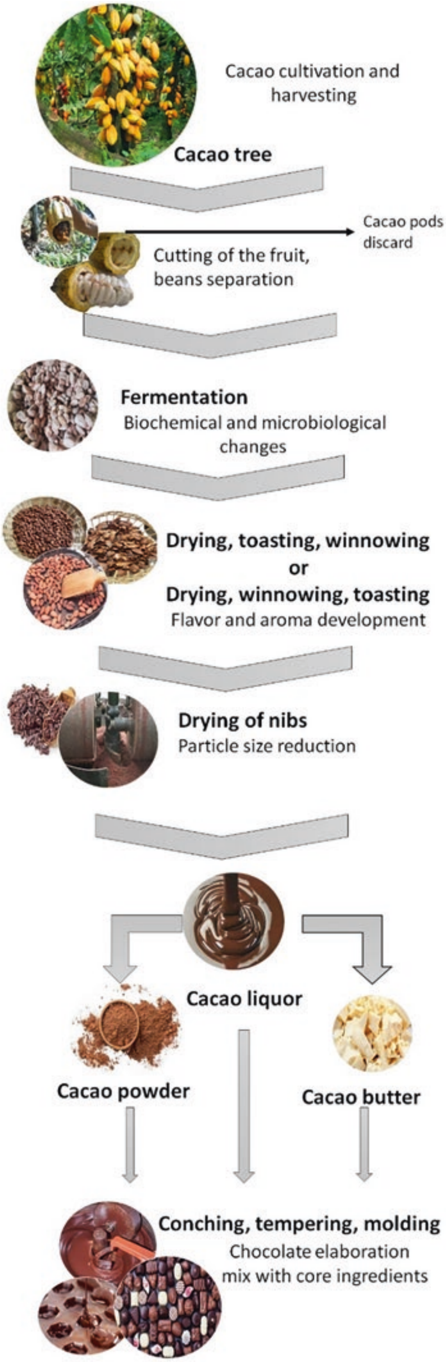
Processing is any operation that transforms agricultural products into a commercial item. During chocolate production, cacao goes through a multi-step process (Fig. 1.2) including harvesting, beans separation from the pods, fermentation, and sometimes roasting, contributing to the development of flavor and aroma of cacao beans. (Gutiérrez, 2017; Tee et al., 2019; Gutiérrez & Pérez, 2015). A cacao pod too ripe may increase the risk of rotting and seed germination, while a pod too unripe may negatively affect the fermentation process. Therefore, to achieve premium cacao flavor from the beans, the pods have to be harvested at the right time.

The maturity stage of cacao is determined by its external pod coloration which, varies according to the genotypes. Thus, coloration is a decisive criterion to taking account by experienced farmers during harvesting to identify the mature cacao. Unripe pods are green, while full ripe pods present different tones. Fully ripe pods may be colored in yellow tones (citrine), orange (amber), red (ruby), violet (amethyst) while, some others might stay in green tones (Gutiérrez, 2017, Tee et al., 2019, Gutiérrez & Pérez, 2015).

In practice, the harvest of cacao is a non-standardized process done about 5 months after the emerging of the pod and coloration changes. However, if the harvested pods are yet in the ripe stage of maturity, it may conduct an over-fermentation; firstly, an anaerobic fermentation inside the pod and aerobic fermentation once the beans are extracted from the pod. This over-fermentation causes excessive proteolysis damaging the precursors of flavor.

The quantification of the secondary metabolites responsible for pigmentation may be a rapid and non-destructive method helpful for cacao pods maturity determination; however, it may be laborious and costly to be done by farmers (Tee et al., 2019). Some researchers have sought techniques that allow establishing homogeneous and standardized ripeness indicators to harvest cacao. Rojas et al. (2020)

Fig. 1.2 General chocolate making process



evaluated physicochemical parameters in three clones cultivated in different Colombia zones to identify potential indicators of cacao maturity. The fruit shape, size, weight, color, moisture, pH, total soluble solids, and titratable acidity. Results point out that as the degree of ripeness progresses, groove depth and apex width are higher; the coloration intensity increased, and total soluble solids increased. While moisture and pH decrease. Each of the clones evaluated presented differences in the parameter through the ripeness process, meaning that ripeness indicators have to be implemented for each cacao variety.

On the other hand, Tee et al. (2019) explored a multiparametric fluorescence sensor to estimate some of these metabolites, such as anthocyanin, flavonol, chlorophyll, and nitrogen, during 5 months across the pod development to determine the optimum harvest period. The non-destructive fluorescence method consisted of scanning the pods with a fluorimeter with six light-emitting diode sources in the UV-A (370 nm) with blue (470 nm), green (516 nm), and red (635 nm) spectral regions. The results showed that flavonols are accumulated in the pods as they developed, contrary to chlorophyll and nitrogen balance, which decrease as they reach maturity. They conclude that both pods and beans harvested at 4 months present quality as good as those harvested at 5 months (Tee et al., 2019).

Despite the ripeness stage is critical to harvest cacao high quality, there is no a standardized method that enables farmers to know the exact time to harvest the fruit. Therefore, for developing a technique to identify the optimal maturity stage of cacao, more studies are needed.

1.3.3.2 Fermentation Process

Raw beans are naturally astringent and bitter in an unpleasant way, the fermentation process lead to biochemical changes necessary for flavor and aroma precursors formation that contribute to the chocolate flavor profile (Santos et al., 2020). Fermentation begins since the selected pods are manually open to remove cacao beans. This process has to be precise to avoid damaging the beans (Aprotosoaie et al., 2016; Gutiérrez, 2017; Rivera-Fernández et al., 2012; Nazaruddin et al., 2006). During fermentation, the cocoa beans undergo physical changes such as the loss of mucilage and their soft and compact texture (Gutiérrez & Pérez, 2015).

In practice, the fermentation is an artisanal and non-controlled process; beans are placed in wooden boxes, sacks, baskets, trays, heaps and plastic containers and subjected to different conditions, which may increase the non-volatile acidity, affecting the quality of the beans (Aprotosoaie et al., 2016; Rivera-Fernández et al., 2012). The length of fermentation may vary depending on the cacao variety, Criollo require 2 or 3 days to fully fermented, while to the Forastero it may take 5–8 days (Rivera-Fernández et al., 2012). The degree of fermentation is measured comparing the color of cut beans to the *Munsell* color chart. Variations on the fermentation conditions affect the pH, titratable acidity, temperature, and enzymatic activity, leading to biochemical changes in phenolics, alkaloids, and nitrogenous compounds influencing the flavor and aroma development (Rivera-Fernández et al., 2012, Nazaruddin et al., 2006).

The mucilaginous pulp (40% of the total fresh weight) that surrounds the cacao beans is the first one to be subjected to the biochemical changes during fermentation due to its richness in glucose, fructose, sucrose, salts, pectin, organic acids, and proteins, hydrolyzed by microorganisms during fermentation. The enzymatic activity varies among the cacao genotypes. Genotypes with high endoprotease and aminopeptidase activity produce better cacao flavor. The pH also influences the enzyme activity; some of the enzymes involved in fermentation are inactivated at a too acid pH, reducing the flavor precursors production. The associated microbial community of cacao beans fermentation is integrated by yeast, bacteria (lactic, acetic, and Bacillus species), and filamentous fungi. Moreover, the microbial activity determines some structural changes promoting the cell constituents (substrates and enzymes) movement (Aprotosoaie et al., 2016; Santos et al., 2020; Leal Jr et al., 2008).

At the first stage of the fermentation process, pulp sugars are hydrolyzed and transformed into ethanol and lactate by yeast and lactic bacteria. However, it is relevant to consider the pulp fraction since an excess of it may decrease the oxygen diffusion, thus, extending the fermentation time, increasing the lactate and ethanol production, and the acidity. Constant removal of the beans during fermentation or partial removal of pulp may reduce this unfavorable effect. Afterward, the second phase of fermentation begins (48–96 h), the aeration increasing, yeast activity is inhibited, and lactic and acetic bacteria are established. All of the biochemical changes performed by microorganisms provoke the loss of membrane permeability, causing the cotyledons' death (Aprotosoaie et al., 2016; Gutiérrez & Pérez, 2015; Leal Jr et al., 2008). At the final stage of fermentation, the substrates are entirely consumed thus, the production of acetic acid ceases increasing the pH up to 5, leading to protein total degradation by endogenous proteases (Aprotosoaie et al., 2016; Leal Jr et al., 2008). The cacao protein composition contains albumin (14–52%) and vicilin (7S)- class globulin (23–43%), which start their hydrolysis after 2-days of fermentation beginning. Albumin is partially hydrolyzed, close to 57% whereas, vicilin (7S)- class globulin is highly hydrolyzed ~90% by aspartic endoprotease and carboxypeptidase. Thus, hydrophobic amino acids (leucine, alanine, phenylalanine, and tyrosine) involved in aroma precursors formation are released (Hue et al., 2016).

Regarding cacao bioactive compounds (Fig. 1.3) three groups are distinguished: (1) flavan-3-ols also known as catechins family (ca. 37%) comprised by (−)-epicatechin, (−)-catechin, (−)-epigallocatechin, (+)-gallocatechin, (+)-epicatechin and (+)-catechin; (2) proanthocyanidins (ca. 58%), comprised by condensed dimers, trimers or oligomers of flavan-3,4-diols being epicatechin the main extension, and (3) anthocyanins (ca.4%), formed by 3-β-D galactosidyl cyanidin and 3-α-L arabinosidyl cyaniding (Gültekin-Özgüven et al., 2016; Lemarcq et al., 2020; Nazaruddin et al., 2006; Rusconi & Conti, 2010; Schinella et al., 2010; Valadez-Carmona et al., 2017). During fermentation, catechins are oxidized by polyphenol oxidase, and their amount is reduced up to 10–20% higher values are considered a sign of non-adequate fermentation. The oxidation of catechins turned the violet cotyledons into

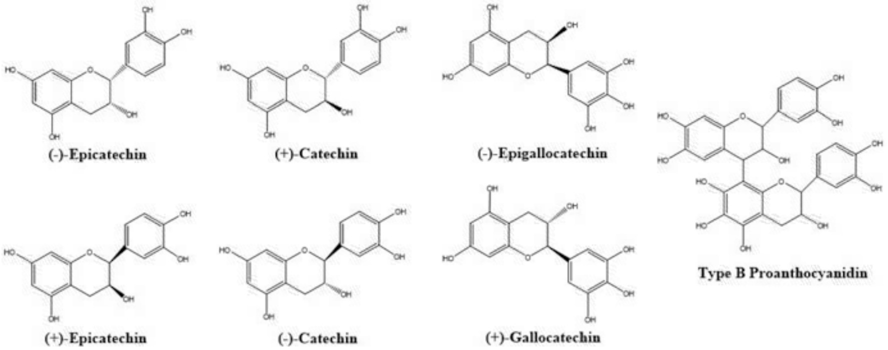


Fig. 1.3 Principal bioactive compounds of cacao beans

the brown characteristic color of chocolate. Proanthocyanidins content decrease 3 to 5 times while anthocyanidins disappear. During the aerobic phase of fermentation, polyphenols are condensed into high molecular insoluble tannins, protein –polyphenol complexes are oxidized. Carbonyl-amino complexes are concentrated reducing the astringency, while alkaloids promote the bitterness development (Gültekin-Özgüven et al., 2016; Nazaruddin et al., 2006; Valadez-Carmona et al., 2017; Plazola-Jacinto et al., 2019).

The pH, temperature and oxygen diffusion contribute to microbial succession throughout the fermentation process. Acidy pH and richness of sugar content allow yeast growing during the first stage. Yeast is the responsible of ethanol production due to pectinolytic enzyme activity. An increase in temperature and aeration contributes to the yeast replacement by lactic acid bacteria (LAB). LAB oxidizes the ethanol to lactic acid, afterwards acetic acid bacteria (AAB) become the dominating microbiota in the fermenting mass and oxidizes the acid lactic to acetic acid. At the end of fermentation spore-forming bacteria growth along filamentous fungi appears on the bean's surfaces. Some of the microorganisms identified from cacao fermentation are: *Kluyveromyces marxianus*, *Saccharomyces cerevisiae var. chevalieri*, *Candida rugopelliculosa*, and *Kluyveromyces thermotolerans*, *Hanseniaspora guilliermondii*, *Pichia kudriavzevii*, *Lactobacillus plantarum*, *Lactobacillus fermentum, Acetobacter pasteurianus* and *Gluconobacter frateurii*. The sequence of the microorganisms' appearance is not well defined yet, it may act simultaneously during fermentation process and even being different depending of the region of origin (Gutiérrez, 2017).

The general activities and composition of each group of microorganisms involved in cacao beans fermentation and responsible for aroma and flavor precursors production are:

Yeast The anaerobic stage of fermentation is conducted by yeast hydrolyzing sugars to produce alcohol and citric acid decomposition to increase pH from 3.5 to 4.2. Some of the yeast involved in cacao bean fermentation process are *Saccharomyces cerevisiae, Hanseniaspora guilliermondii, H. uvarum, Pichia kluyveri, P. membra-*

nifaciens, P. fermentans, I. orientalis, Candida torulopsis, C. silvae, C. zemplinina, C. diversa, C. stellimalicola, and Schizosaccharomyces spp.

Lactobacilli This group of bacteria acts in the second stage of the fermentation when increase the aeration, the LAB activity is not limited to produce lactic acid by metabolizing glucose they also participate in the assimilation of citric acid to rise pH. Little LAB has identified from cacao beans fermentation, some of them are *Lactobacillus, Leuconostoc, Lactococcus,* and *Pediococcus* genera *Lactobacillus collinoides, L. mal'ı, L. hilgardii, L. fermentum,* and *L. plantarum* species.

Acetic Acid Bacteria The AAB transforms the ethanol produced by yeast into acetic acid during aerobic stage, this group of microorganism acts after increase in temperature and aeration. Some species found during cacao fermentation are: *Acetobacter pasteurianus, A. aceti, A. syzygii, A. tropicalis, A. malorum, Gluconobacter oxydans,* and *G. xylinus.*

However, these species have shown insufficient activity in natural conditions. Thus, an artificial inoculum of yeast with pectinolytic enzymes would be an option when cacao beans are rich in pulp to small or large-scale process (Leal Jr et al., 2008). Under laboratory scale *S. cerevisiae* var. *chevalieri* and *Kluyveromyces fragilis* have shown good pectinolytic activity improving fermentation and final product quality. Therefore, to improve the cacao beans fermentation, the use of specific strains has been evaluated. *Kluyveromyces marxianus hybrid* strain with high pectinolytic activity was inoculated at a rate equivalent to 2.6×10^6 cell kg^{-1} of cacao beans (Aprotosoaie et al., 2016; Camu et al., 2008; Hansen et al., 2000). The fermentation with *K. marxianus* showed better sensorial attributes, less acidity, more degradation of proteins and beans with appropriate brown color than naturally fermented beans. Sande Santos evaluated the effect of different strains on cacao Scavina fermentation, finding that *Candida parapsilosis*, *Torulaspora delbrueckii*, and *Pichia kluyveri* are the ones with relevant activity on flavor precursors production.

However, along with the cacao processing in temperate and humid conditions, fungi may proliferate and produce several secondary metabolites such as mycotoxins that contaminate the cacao beans or their derived products (chocolates or powders) (Akinfala et al., 2020; Copetti et al., 2013). Ochratoxin A (OTA) is one of the mycotoxins detected in cacao derived products. OTA is produced by *Aspergillus carbonarius* and *Aspergillus niger,* and *Penicillium* fungi genera. OTA exhibits immunotoxicity, neurotoxicity, and teratogenic effects that affect kidney and liver health (Brera et al., 2011; Copetti et al., 2013; Mishra et al., 2015). In 2001, the joint FAO/WHO Expert Committee on Food Additives (JECFA 2001) established the tolerable maximum limit intake at 100 ng/kg body weight. In 2003 the Italian Ministry of Health claims a maximum limit for OTA in cacao powder and cacao derived products at 0.5 μg/kg and 2 μg/kg respectively, contrary to the European Union that declares cacao-derived products as non-significant contributors of OTA intake. Brera et al. (2011), evaluated 300 samples of cacao and chocolate-based products for sale in the Italian market, finding that 179 were positive for OTA presence. Still, the content was below the Italian limits. Since the results suggested that OTA exposure through cacao-derived products consumption is not a significant health concern the Italian Superior Council of Health decided to adopt the European legislation.

On the other hand, Akinfala et al. (2020) assessed the fungal profile and fungal metabolites patterns of Nigerian cacao beans. Citrinin mycotoxin was detected on fermented beans, and unexpectedly OTA was not detected. It is the first time that citrinin was detected in fermented beans, and it is a health concern due to as same as OTA is also a potent nephrotoxin.

More than 60% of cacao-derived products present OTA at different levels, consequently these products may not be exported or inclusive may be rejected if exceeds the permissible limits established in legislations. Thus, it is necessary the analysis for OTA during all the processing stages of cacao beans and cacao derived products (Mishra et al., 2015). The current analytical techniques, used to detect OTA are high performance liquid chromatography (HPLC) adapted with fluorescence detectors, gas chromatography-mass spectrometry, enzyme linked immunosorbent assay (ELISA), and thin layer chromatography (TLC). However, OTA on-site detection is difficult to perform by farmers or small producers. In this context, a new technique for OTA detection was developed by Mishra. The use of an electrochemical impedimetric aptasensor allowed a rapid detection and quantification for OTA. The aptasensor showed 0.15 ng/mL as the limit of detection (LOD) besides good selectivity and reproducibility. Therefore, a suitable and sensitive analytical technique selection joint of good sampling may facilitate the OTA detection in all process stages of cacao.

1.3.3.3 Drying

After fermentation, the cocoa beans must be dried to (1) reduce the moisture extending the shelf life, (2) avoid the spoiling, (3) complete the oxidation began in fermentation, and (4) facilitate their transport to industry. The oxidation of polyphenols is achieved during drying; polyphenols are oxidized to quinones which condensates with free amino acids and sulfhydryl groups developing brown polymers.

After drying, the cacao beans are dried about 7 days to reduce moisture by 7–8%, and the water activity must be below 0.7 to avoid spoiling during storage. The drying process should be slow to reduce astringency, bitterness and, acidity; too fast drying generates beans highly acid (Gültekin-Özgüven et al., 2016; Gutiérrez & Pérez, 2015). Sun-dried is the traditional method to dry cacao beans because it develops a more marked chocolate flavor. However, it sundried takes a long time, low production rate, and may cause environmental contamination. Therefore, to avoid contamination artificial drying with acceptable manufacturing practices must be implemented. Therefore, hot air drying is an optional method that avoid exposition of environmental conditions, whereas the drying temperature is controlled and standardized.

Once the drying process ends cacao beans are cleaned, selected and kept in sacks around 60–65 kg in a ventilated warehouse, then transported to continue the processing.

1.4 Chocolate Manufacture and Factors Affecting Its Quality

1.4.1 Roasting

Roasting process goals are (1) to reduce the moisture content (<2%), (2) to facilitate the loss of hulls, (3) to reduce the acidity, and (4) to develop the flavor and color of chocolate. Roasting consists of high temperatures application (120–150°C) to create the characteristic chocolate color and flavor. However, the use of high temperatures might have a detrimental effect on the antioxidant properties and nutritional value of the final product (Gutiérrez & Pérez, 2015; Lemarcq et al., 2020; Zzaman et al., 2014). For example, lipid oxidation and non-enzymatic browning are promoted by high temperatures, besides the loss of essential fatty acids and essential amino acids. Consequently, the health benefits associated with cacao consumption are affected negatively (Djikeng et al., 2018; Gutiérrez, 2017).

The roasting process may be done on the whole bean (including hulls) or only on the nib (dehulled). The whole-bean roasting makes the hull separation easier and breaks into nibs (small pieces of cacao without hull). During roasting the beans size is highly important, small beans might be burned and too large beans might have an incomplete roasting in the center. In addition, during roasting the cacao butter partially melts and migrates to the hull (4–6%) resulting in losses during winnowing (Gutiérrez, 2017).

On the other hand, before the roasting nib has to be pre-treated to easier the hull removal which, consists of heat quickly the beans' exterior at high temperatures to avoid chemical reactions that might modify the flavor. Once the hull is removed, the roasting is performed by two procedures: (1) roasting the small pieces obtained after dehulling or (2) milling the nibs into cacao mass or liquor before roasting (Gutiérrez, 2017). For nibs roasting, moisture has to be controlled since during milling, the nib mass acts as a liquid, and moisture near to 10% makes the system cellulose-protein-fat might turn too rigid hindering the mill.

During roasting the biochemical reactions that started in fermentation are finished; the aroma and flavor precursors (free amino acids, oligopeptides, and reducing sugars as glucose and fructose) interact non-enzymatic browning Maillard reactions to develop the characteristic and desired chocolate flavor. Volatile compounds such as glucosyl amines and fructosyl amines are formed by the reaction of a free amino group of amino acids and reducing sugars reactive carbonyl (Schiff bases), which undergo tautomerization 1,2 enaminols and 1-amino-1-deoxy-2--ketoses (rearrangement to Amadori compounds). The amino compounds are decomposed to 3-deoxyhexuloses turning them into hydroxymethylfurfurals and furfural derivatives by loss of water. Maltol, isomaltol and α-dicarbonyl compounds are formed by 2,3-enediol and dehydroreductone intermediates at neutral or basic pH. The subsequent dehydration and transamination of α-dicarbonyl into small aldehydes and ketones is crucial for chocolate flavor development. The pyrroles and pyridines formed via Strecker degradation polymerized into brown melanoidins pigments (Aprotosoaie et al., 2016; Gutiérrez, 2017). During roasting, some flavor notes are developed by particular interactions. For example, the "sweet chocolate" note is generated by leucine and glucose reaction, "chocolate" notes by threonine, glutamine, and glucose reaction, and nut and cacao flavors by aldehydes and pyrazines. As for aroma regards, those with floral notes are produced by aromatic phenylacetaldehyde or by linalool.

During roasting non-volatile compounds derived from alkaloids (methylxanthines, polyphenols, and proteins are also formed. The specific and characteristic bitterness of roasted cacao beans is provided by adducts formed between diketopiperazines and methylxanthines. The high temperatures of roasting cause structural modifications like epimerization on flavanol monomers, dimers, trimers and highly possible procyanidins. The epimerization of (−)-epicatechin to (−)- catechin, and (+)-catechin to (+)-epicatechin suggest the presence of the four catechins in cacao powders and chocolate. The epimerization may have positive effect on the bioavailability and absorption due to in the particular case of catechin, it has been reported that (+)-isomer absorption is favored compared to the (−)-isomer (Aprotosoaie et al., 2016; Kothe et al., 2013; Hurst et al., 2011).

Compounds formed during roasting that contributes to chocolate flavor development belong to the following chemical families: aldehydes, ketones, alcohols, pyrazynes, esters, quinoxalines, furans, lactones, pyrroles, pyrones, and diketopiperazines and are summarized in Table 1.1.

During roasting non-volatile compounds that do not participate on cacao flavor development are also produced. Some of these compounds are biogenic amines such as 2-phenylethylamine, tyramine, tryptamine, serotonin, and dopamine, which have a vital role in the mood-enhancing effect cacao (Aprotosoaie et al., 2016; Oracz & Nebesny, 2014).

Although roasting is essential to develop the characteristic chocolate flavor and aroma, it has a detrimental effect on polyphenolic content (Aprotosoaie et al., 2016; Djikeng et al., 2018; Hii et al., 2017; Lemarcq et al., 2020). Therefore Zzaman et al. (2014) proposed the superheated steam application as an alternative method to roast cacao beans and thus, reduce the degradation of polyphenols. Superheat steam is a suitable method to roast cacao beans with better total phenolic content preservation than hot air and a short time process.

Table 1.1 Cocoa main odor-flavor volatile compounds identified in roasted cacao beans

Compound	Odor description	Flavor perception
Alcohols		
1-Propanol	Sweet, candy	Sweet chocolate
2-Methyl-1-butanol	Fruity, grape	Fruity
2,3-butanediol	Cacao butter	Sweet chocolate
2-Pentanol	Green, mild Green	Vegetal
1-Hexanol	Fruity, green	Fruity, herbal
2-Hexanol	Fruity, green	Fruity, herbal
Trans-3-hexen-1-ol	Grassy, green	Vegetal
2-Heptanol	Citrusy	Fruity
1-Phenylethanol	Honey, floral	Floral
2-Phenylethanol	Honey, floral	Floral
Benzyl alcohol	Sweet, floral	Floral
3-Methyl-1-butanol	Malty	Chocolate
2-Ethyil-1-hexano		
2-Nonanol		
1,3-butanediol		
Aldehydes and ketones		
2-Phenyl acetaldehyde	Honey, floral	Floral
2-Methylpropanal	Chocolate	Sweet chocolate
2-Phenylpropanal	Floral	Floral
2-Methylbutanal	Chocolate	Sweet chocolate
3-Methylbutanal	Chocolate	Sweet chocolate
2-Phenyl-2-butenal	Sweet	Sweet chocolate
4-Methyl-2-phenyl-2-pentenal	Cocoa	Sweet chocolate
5-Methyl-2-phenyl-2-hexenal	Cocoa	Sweet chocolate
2-Nonenal	Green	Herbal
2-Pentanone	Fruity	Fruity
2-Heptanone	Fruity, floral	Fruity, floral
Acetophenone	Floral	Floral
2-Hydroxy acetophenone	Heavy floral, herbaceous	Floral, herbal
4-Methyl acetophenone	Fruity, floral	Fruity, floral
2-Isopropyl-5-methyl-2-hexenal		
Benzaldehyde		
2,3-Butanedione	Buttery	Buttery

(continued)

Table 1.1 (continued)

Compound	Odor description	Flavor perception
Acetoin	Buttery	Creamy
2-Nonanone	Flowery,	Fatty
1H-inden-1-one-2,3 dihydro		
n-Hexanal	Green	Herbal
Acids		
2-Methylpropionic acid	Floral	Floral
3-Phenylpropionic acid	Sweet, rose	Floral
Phenols		
Vanillin	Chocolate, sweet, vanilla	Sweet chocolate
Cinnamic acid	Honey, floral	Floral
2-Methylphenol	Smoky	
Phenol	Smoky	
4-Methyl phenol	Smoky	
3-Methyl phenol		
Esters		
Ethyl acetate	Pineapple	Fruity
Isobutyl acetate	Fruity	Fruity
Isoamyl acetate	Fruity, banana	Fruity
Benzyl acetate	Floral, jasmine	Floral
Methylphenyl acetate	Sweet, honey, jasmine	Floral
Ethyl phenyl acetate	Fruity, sweet	Floral
2-Phenylethyl acetate	Honey, floral	Floral
Ethyl butyrate	Pineapple	Fruity
Ethyl lactate	Fruity	Fruity
Diethyl succinate	Pleasant aroma	Floral
Ethyl 2-methylbutanoate	Fruity	Fruity
Ethyl 3-methylbutanoate	Fruity	Fruity
Ethyl valerate	Fruity, apple	Fruity
Ethyl hexanoate	Fruity	Fruity
Ethyl octanoate	Fruity, floral	Fruity
Ethyl decanoate	Pear, grape	Fruity
Ethyl laurate	Fruity, floral	Fruity, floral
Isoamyl benzoate	Balsam, sweet	Floral
Methyl salicylate	Bitter almond	Nutty
Methyl cinnamate	Balsamic, strawberry	Fruity
Ethyl cinnamate	Sweet, cinnamon like	Sweet chocolate
Methyl acetate		
Butyl acetate		
3-Methyl-1-butanol acetate	Banana	

(continued)

Table 1.1 (continued)

Compound	Odor description	Flavor perception
2-Heptanol acetate		
Ethyl octanoate	Floral	Fruity
2-Methyl-propanoic acid ethyl ester		
Butyrolactone	Bready	
Ethyl dodecanoate	Floral, pear, grape	Fruity
1,3-Propanediol diacetate		
Benzoic acid ethyl ester		
Amines, amide, nitriles, purines		
Benzonitrile	Almon	Nutty
N-(2-phenethyl) formamide	Essences	Floral
Lactones		
γ-Decalactone	Coconut	Nutty
δ-Octenolactone	Peach	Fruity
Terpenoids		
Geraniol	Floral, rose, fruity	Floral, fruity
Geranyl acetate	Rose, lavender	Floral
α-Terpenyl formate	Herbaceous, citrus	Herbal, fruity
Linalool (cis-pyranoid)	Floral, green	Floral, herbal
Linalool (trans-pyranoid)	Floral	Floral
Linalool oxide (cis-furanoid)	Nutty	Nutty
Linalool oxide (trans-furanoid)	Floral, citrus	Fruity, floral
β-myrcene		
Furans, furanones, pyrans, pyrones		
2-Furfural	Almond	Nutty
5-Methyl-w-furfural	Sweet, caramel	Sweet chocolate
2-Furfuryl acetate	Fruity, banana	Fruity
2-Acetylfuran	Sweet, balsamic, slightly coffee	Sweet chocolate
2-Aceryl-5-methylfuran	Strong nutty	Nutty
2-Furfuryl propionate	Spicy, floral	Floral
5-(1-Hydrohyethyl)-2-furanone	Red fruit, jam, green notes	Fruity, herbal
Dihydro-3-hydroxy-4,4-dimethyl-2-furanone	Coconut	Nutty
4-Hydroxy-2,5-dimethyl-3-(2H) furanone (furaneol)	Fruity, strawberry, hot sugar	Fruity, nutty
3-Hydroxy-2-methyl-4-pyrone (maltol)	Roasted nuts	Nutty
5,6-Dihydro-6-pentyl-2-pyrone	Coconut	Nutty
3-Furfuryl alcohol	Bready	
Pyrroles		
Pyrrole	Nutty	Nutty
2-Acetylpyrrole	Chocolate, hazelnut	Sweet chocolate

(continued)

Table 1.1 (continued)

Compound	Odor description	Flavor perception
Pyrrole-2-carboxalehyde	Nutty	Nutty
(1-ethyl-2-pyrrolidinyl)-methanol		
1-(1H-pyrrol-2-yl) ethanone	Chocolate, hazelnut	
Pyrazines		
2-Methylpyrazine	Nutty, chocolate, cocoa, roasted nuts	Sweet chocolate
2-Ethylpyrazine	Peanut, butter, musty nutty	Nutty
2,5-Dimethylpyrazine	Cocoa, rusted nuts	Sweet chocolate
2-6-Dimethylpyrazine	Nutty, coffee, green	Nutty, herbal
2-Ethyl-5-methylpyrazine	Nutty, raw potato	Nutty, herbal
2,3-Diethylpirazine	Nutty, hazelnut, cereal	Nutty
2,3,5-Trimethylpyrazine	Cocoa, rusted nuts, peanut	Sweet chocolate
2,3,5,6-Tetramethylpyrazine	Chocolate, cocoa, coffee	Sweet chocolate
2,3,5-Trimethyl-6-ethylpyrazine	candy, sweet	Sweet chocolate
2,3-Dimethylpyrazine	Caramel, cocoa, sweet, baked	
2-Ethyl-6-Methyl pyrazine		
Trimethylpirazyne	Earthy, cocoa, fried	
3-Ethyl-2,5-Dimethyl pirazine	Roasted, smoky	
2,3-Dimethyl-5-ethyl pyrazine	Roasted, chocolate	
Tetramethyl pyrazine	Roasted, cocoa, chocolate	
Hydrocarbons		
2,3- Dimethylheptane		
1-Ethyl-2-methylbenzene		
Styrene		
n-Butylbenzene		
Naphtalene		

Adapted from Aprotosoaie et al. (2016), Marseglia et al. (2020)

1.4.2 Grinding

After roasting, cacao beans are grinding to small the particle size and fat obtention for chocolate preparation. An essential aspect of chocolate is to be solid at room temperature (20–25 °C) and "melt in the mouth" (37 °C). If the cacao beans are coarsely milled the texture turns granular and not palatable lowering its acceptance (Gutiérrez & Pérez, 2015). The particle size must be reduced to an optimum average of 0.5 to less than 30 microns to enhance the chocolate palatability. For optimum particle size, beans are milled twice, firstly with an impacting mill, a liquid is obtained due to the met of beans fat. After that, to act on the liquid a ball mill is used, and the remainder big particles are trapped between the balls and then broken during ball rotation; the degree of grinding depends on the balls' diameter. After the particle size reduction, the cacao liquor is kept in stainless steel tanks at 40–45° until the next step of the process. At the same time, the paste is packaged in high-density polyethylene bags to avoid contamination.

1.4.2.1 Butter and Powder Cacao Obtention

After the cacao nibs' ground, the obtained product is a fluid mass or liquor comprised of cacao and cacao butter. The cacao butter composition is glycerolipids (~97%), unsaponifiable matter (~3%), and traces of diglycerides, monoglycerides, and phospholipids. The saturated fatty acids (FA) finding in cacao butter is palmitic acid (38%) and stearic acid (29%), while the unsaturated acids finds are oleic acid (28%) and linoleic acid (2%) (Jahurul et al., 2013; Servent et al., 2018). Cacao butter extraction from the liquor has been performed by a hydraulic press, mechanical press, screw presses, supercritical fluid extraction (SFE), and solvent extraction methods. The hydraulic press, mechanical press, and screw presses methods are the most used in the industry at40 to 50 MPa; however, they do not extract enough cacao butter yield and affect the nutritional properties (Jahurul et al., 2013).

The nibs' initial butter content is 55% and it is reduced more than a half through the pressing process the rest of the butter is retained by the cacao press cake. On the other hand, an opaque and low-quality butter is obtained if unhulled cacao beans are pressed; however, this is common to handle beans with insufficient fermentation or inadequate drying or roasting (Gutiérrez & Pérez, 2015; Gutiérrez, 2017). Therefore, the chocolate industry criteria to purchase the butter are: (1) a free tatty acid content below 1.75%, (2) 0.5% of saponification value (indicates the average chain length), (3) iodine value (the higher the iodine values, the greater the softness) (4) acid value (free fatty acids quantification) and (5) cloud point (the higher unsaturation the lower cloud point (Gutiérrez & Pérez, 2015, Gutiérrez, 2017, Jahurul et al., 2013).

Cacao powder (or cocoa) is obtained from the cacao press cake left after butter extraction. Fragments of 3 cm are formed and cooling further milling into powder. For low fat or free-fat cacao-derived products, the non-fat powder is used (Gutiérrez & Pérez, 2015, Gutiérrez, 2017). Derived from the increasing demand for cacao and cacao-derived products, some traders partially substitute the cacao powder with carob powder, which has marked aromatic and visual similarity to cacao. Near-infrared spectroscopy (NIR) has demonstrated an effective and rapid method to detect cacao alteration with carob powder and a useful tool for cacao merchants to ensure that cacao powder is free of adulteration (Quelal-Vásconez et al., 2018).